

Metal and Metal Oxide-Supported Platinum Monolayer Electrocatalysts for Oxygen Reduction

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Objectives

The objective of this research is to demonstrate the possibilities of synthesizing platinum monolayers as electrocatalysts for the oxygen reduction reaction (as well as methanol and ethanol oxidation) using metal, metal oxide, metal alloy, and pyrochlore as single crystal, and homogenous or core-shell nanoparticle substrates. In addition, we will study alloying palladium to make it as active catalyst as platinum. Employing a combination of experimental techniques and computational methods, we plan to develop a fundamental understanding of the atomic-scale phenomena in platinum monolayer-substrate systems, and enhance our understanding of the platinum-substrate interactions and origin of the electronic and catalytic properties of Pt.

Technical Barriers

The project is focused on synthesizing Pt monolayers as electrocatalysts for fuel cell reactions, using metals and metal alloys less expensive than Pt, metal oxides, as single crystal, homogenous and noble metal – non-noble metal core-shell nanoparticle substrates. Fundamental understanding of the structure and catalytic activity of Pt-substrate systems should help overcome several technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program. These include i) Costs of electrocatalysts, i.e. electrodes; ii) Electrode performance and iii) Durability.

Abstract

We demonstrated the synthesis of a new type of electrocatalysts for the O₂ reduction reaction (ORR)

consisting of Pt monolayers on suitable metal or alloy nanoparticles. They can have enhanced activities and an ultra low Pt content. Thus, they offer a very promising way to resolving some deficiencies of the existing fuel cell technology, in particular the inadequate efficiency of energy conversion and the high Pt content of electrocatalysts. Enhanced activity of Pt was ascribed to a strain in Pt monolayer, which causes a shift of the d-band center of Pt, electronic (ligand) effects, and a shift of Pt oxidation to positive potentials. The most interesting recent results include: i) Pt_{ML}/Au/Ni₅/C catalyst that showed the highest activity reported so far for the ORR on high surface-area samples with the half-wave potential of 0.895V vs. RHE at room temperature; ii) The electrodeposition of Pt on RuO₂(110) starts with the deposition of submonolayer, then the growth of Pt islands, in a manner similar to the Stranski-Krastanov mode; iii) NbO₂ affords excellent support for Pt as the ORR and methanol oxidation, having an unsurpassed stability in acids, and apparently, providing additional M-OH sites for CO oxidation; iv) Intrinsic Pd surfaces bind oxygen too firmly to allow efficient removal of the adsorbed reaction intermediates, we predicted, and demonstrated that reducing its reactivity as in a Pd₃Fe(111) alloy, would result in very active catalyst because of its moderate interaction with oxygen; and v) We demonstrated that small Au clusters affect the properties of the underlying metal surfaces. Moreover, platinum oxygen reduction fuel cell electrocatalysts can be stabilized against dissolution under potential cycling regimes (a continuing problem in vehicle applications) by modifying Pt nanoparticles with gold clusters.

Progress Report

Further work on mixed-metal Pt monolayer electrocatalysts comprising the Pd-supported Pt-M mixed monolayers, with M strongly adsorbing OH or O, entailed verifying the concept of reduced PtOH coverage due to adsorbate-adsorbate repulsion involving the oxide species. The results of *in situ* x-ray absorption near edge spectroscopy (XANES) studies verified that the origin of high ORR activities for these electrocatalysts was due to reduced formation of PtOH. New classes of the platinum monolayer ORR electrocatalysts were synthesized, including: Pt monolayer on non-noble metal - noble metal core-shell nanoparticle electrocatalysts, Pt monolayer electrocatalysts on an NbO₂ support, Pt monolayer electrocatalysts on a RuO₂(110) support and the synthesis of CoWO₄ single crystal bronze has been accomplished.

The work with Pt monolayer on non-noble metal - noble metal core-shell nanoparticle electrocatalysts involved efforts to further lower the noble metal content by improving the synthesis of core-shell nanoparticles. We achieved well-controlled electroless deposition of Au on Ni(111) from a solvent/surfactant ethylene glycol. Weakly ordered Au deposits were obtained after a quick annealing, which was verified by atomically resolved STM images. The segregation of Au in AuNi₅ was clearly evident using a micro-powder x-ray diffraction technique, TEM, and EDS. EDS in nano-probe mode, was used to obtain a cross-sectional distribution of Pt, Au, and Ni in Pt/Au/Ni nanoparticle. The Pt_{ML}/Au/Ni₅/C catalyst showed the highest activity reported so far for the ORR on high surface-area samples with the half-wave potential of 0.895V vs. RHE at room temperature (Figure 1).

We developed a method to express both kinetic equation and adsorption isotherm for the reaction intermediate in terms of free energies of adsorption and activation for the elementary reactions. Further investigation of a monolayer of Pt deposited on the surfaces of NbO₂ nanoparticles involved XANES *in situ* studies, and tests of Pt/NbO₂ catalyst for methanol oxidation. Further characterization of a Pt monolayer on NbO₂ indicated a shift in the PtOH formation to positive potentials. It is quite feasible that H₂O, or OH chemisorbed on NbO₂ play that role. These results indicate that NbO₂ affords excellent support for Pt, having an unsurpassed stability in acids, and apparently, providing additional M-OH sites for CO oxidation.

We demonstrated that small Au clusters affect the properties of the underlying metal surfaces. Moreover, platinum oxygen reduction fuel-cell electrocatalysts

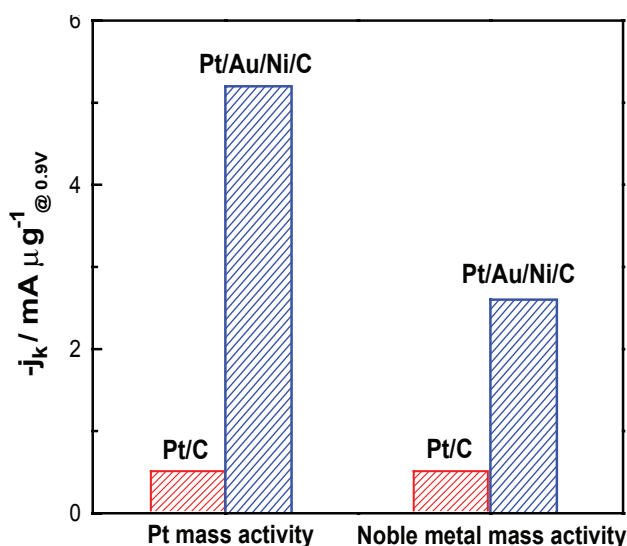


FIGURE 1. Pt and total noble metal mass activity of Pt_{ML}/Au/Ni₅/C and commercial Pt/C for the ORR in 0.1 M HClO₄ at 0.9V. An eight-fold enhancement in activity is observed.

can be stabilized against dissolution under potential cycling regimes (a continuing problem in vehicle applications) by modifying Pt nanoparticles with gold clusters. *In situ* XANES and voltammetry data suggest that the gold clusters confer stability by raising the Pt's oxidation potential (Figure 2). Possibly Au atoms block kink and step sites of Pt where dissolution starts. Our DFT calculations show that Au clusters-induced local surface relaxation (contraction) can occur. That can generate a similar effect. Surface x-ray scattering will be used to verify this new type of surface relaxation. We developed a method to express both kinetic equation and adsorption isotherm for the reaction intermediate in terms of free energies of adsorption and activation for the elementary reactions. Both polarization curves and the adsorption isotherm of the HOR intermediate (H_{HOR}) were analyzed to study the effects of the underpotentially deposited H (H_{UPD}) on the HOR kinetics. With the lateral repulsion determined by DFT calculations and the adsorption isotherm for the HUPD obtained experimentally, we found that the inactive HUPD affected the adsorption isotherm for the HHOR, but had little effect on the activation free energies for adsorption.

Future Directions

Further studies of Pt monolayer electrocatalysts will focus on obtaining a fundamental understanding of their atomic-scale phenomena, thereby to optimize the interaction of Pt with substrates thus maximizing the catalysts' activity and stability. We will continue to improve synthetic methods for the core-shell nanoparticles described above. Tungsten bronzes and Magneli phases will be characterized and used as supports for Pt monolayers. In addition, we will study the single crystal alloys and noble metal-non-noble metal

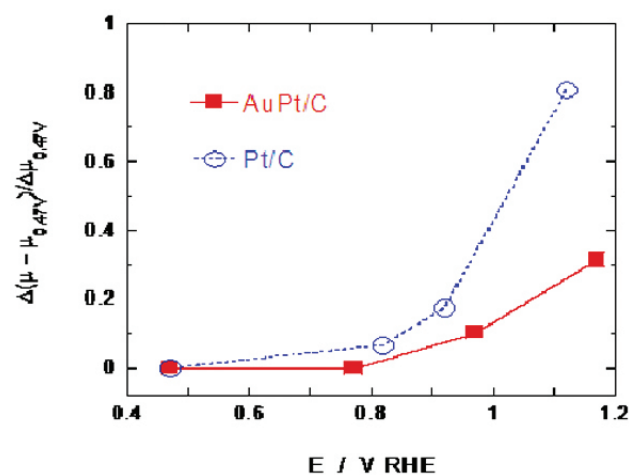


FIGURE 2. X-ray absorption intensity for AuPt/C (Pt protected by Au) and commercial Pt/C as a function of potential normalized by the value at 0.47V where Pt is not oxidized. Considerably lower oxidation of Pt gives smaller absorption inten

shell-core nanoparticles as supports to improve the Pt monolayer's activity for the ORR. Combining the state-of-the-art experimental techniques and computational chemistry methods will help reaching that goal. A new method for controllable metal monolayer deposition on oxides (both, conductive and non-conductive) will be developed. It involves the adsorption of cations (Pb, Zn or Bi) on oxides, followed by reduction of cations and displacement of the thus formed neutral atoms by Pt. This method opens unprecedented possibilities for metal deposition on oxide surfaces. We will resume work on electrocatalysis for methanol oxidation and we will study in detail the effects of Au clusters on the underlying supports, in particular in relation to stabilizing Pt using UHV techniques, electrochemistry and DFT. Thin-films of pyrochlore oxide will be synthesized to quantify the surface dissolution in acidic medium. We will determine the ORR activity of thin-film pyrochlore oxides in alkaline and acidic medium.

Publications 2006-2007

1. M.H. Shao, P. Liu, R.R. Adzic, Superoxide is the intermediate in the oxygen reduction reaction on platinum electrode. *J. Am. Chem. Soc.* 128 (2006) 7408-7409.
2. M.H. Shao, K. Sasaki, R.R. Adzic, Pd-Fe nanoparticles as electrocatalysts for oxygen reduction. *J. Am. Chem. Soc.* 128 (2006) 3526.
3. Ping Liu, James T. Muckerman, Radoslav R. Adzic, Adsorption of Platinum on the stoichiometric RuO₂(110) surface, *J. Chem. Phys.* 124 (2006) 141101.
4. Jia X. Wang, Thomas E. Springer, Radoslav R. Adzic, Dual-Pathway Kinetic Equation for the Hydrogen Oxidation Reaction on Pt Electrodes, *J. Electrochem. Soc.* 153 (2006) A1732.
5. B. Vukmirovic J. Zhang, K. Sasaki, F. Uribe, M. Mavrikakis, R. R. Adzic. Platinum Monolayer Electrocatalysts for Oxygen Reduction, *Electrochim. Acta*, 52 (2007) 2257.
6. M.H. Shao, T. Huang, P. Liu, J. Zhang, K. Sasaki, V.B. Vukmirovic, R. R. Adzic, Palladium Monolayer- and Palladium Alloy- Electrocatalysts for Oxygen Reduction, *Langmuir* (Electrochemistry special issue) 22 (2006) 10409
7. F.H.B. Lima, J. Zhang, M. H. Shao, K. Sasaki, M. B. Vukmirovic, E. A. Ticianelli, R. R. Adzic, Catalytic Activity - d-band Center Correlation for the O₂ Reduction Reaction on Pt in Alkaline Solutions, *J. Phys. Chem. C*, 111(2007) 404.
8. J. Zhang, K. Sasaki, E. Sutter, R. R. Adzic, Stabilization of Platinum Oxygen Reduction Electrocatalysts Using Gold Clusters, *Science*, 315 (2007) 220.
9. Minhua Shao, Ping Liu, Junliang Zhang, Radoslav Adzic Origin of Enhanced Activity in Palladium Alloy electrocatalysts for Oxygen Reduction Reaction, *J. Phys. Chem. B* (special issue) submitted.
10. R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J.X. Wang, A.U. Nilekar, M. Mavrikakis, J. A. Valerio, F. Uribe, Platinum Monolayer Fuel Cell Electrocatalysts, *Topics in Catalysis* (special issue) in press.
11. F.H.B. Lima, J. Zhang, M. H. Shao, K. Sasaki, M. B. Vukmirovic, E. A. Ticianelli, R. R. Adzic, Pt monolayer electrocatalysts for O₂ reduction: PdCo/C substrates-induced activity in alkaline media, *J. Solid State Electrochem.* (special issue) submitted.
12. A.U. Nilekar, Y. Xu, J. Zhang, M.B. Vukmirovic, K. Sasaki, R.R. Adzic, M. Mavrikakis, Bimetallic and Ternary Alloys for Improved Oxygen Reduction Catalysis, *Topics in Catalysis* (special issue) submitted.

Book Chapter

13. N.S. Marinkovic, M.B. Vukmirovic and R.R. Adzic, Some Recent Studies in Ruthenium Electrochemistry and Electrocatalysis, *Modern Aspects of Electrochemistry*, C. Vayenas, R. White, M. Gamboa-Adelso, Editors, Vol. 42, 2006, Springer 2007 (New York).in press.

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14. W. Mustain and J. Prakash, A Model for the Electroreduction of Molecular Oxygen, *J. Electrochem. Soc.* 2006 (submitted).
15. W. Mustain and J. Prakash, Kinetics and Mechanism for the Oxygen Reduction Reaction on Polycrystalline Cobalt-Palladium Electrocatalysts in Acid Media, *Electrochim. Acta.*, 2006 (submitted).

Patent Applications Adzic et al.

1. Synthesis of Metal-Metal Oxide Catalysts and Electrocatalysts Using a Metal Cation Adsorption/Reduction and Adatom Replacement by More Noble Ones
2. Electrocatalyst for ethanol oxidation at fuel cell anodes
3. Electrocatalyst for Oxygen Reduction Protected Against Oxidation and Dissolution